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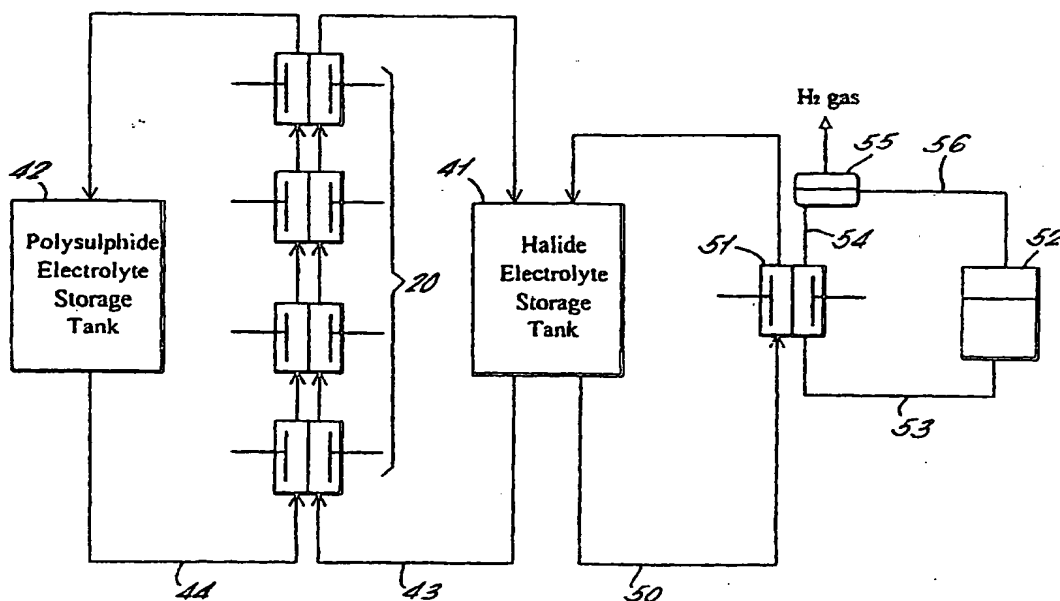
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(54) Title: ELECTROLYTE REBALANCING SYSTEM

(57) Abstract: A process for rebalancing the electrolyte system in a regenerative fuel cell using a sulfide/polysulfide reaction in one half of the cell and a bromine/bromide reaction in the other half of the cell comprises passing the electrolyte containing sulfide/polysulfide or bromine/bromide through the +^{ve} chamber of an auxiliary cell and passing an electrolyte containing water and being free from polysulfide or bromine through the -^{ve} chamber of the auxiliary cell, the auxiliary cell operating so as to oxidise sulfide ions to sulfur or bromide ions to bromine in the +^{ve} chamber and to reduce water to hydrogen and hydroxide ions in the -^{ve} chamber.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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Electrolyte Rebalancing System

The present invention relates to the field of
regenerative fuel cell (RFC) technology. In
5   particular it relates to apparatus and methods for the
operation of RFCs which enhance their performance
characteristics.

The manner in which RFCs are able to store and deliver
10   electricity is well known to those skilled in the art.
An example of an RFC is described in US-A-4485154
which discloses an electrically chargeable,
anionically active, reduction-oxidation system using a
sulfide/polysulfide reaction in one half of the cell
15   and an iodine/iodide, chlorine/chloride or
bromine/bromide reaction in the other half of the
cell. The two halves of the cell are separated by a
cation exchange membrane.

20   The overall chemical reaction involved, for example,
for the bromine/bromide-sulfide/polysulfide system is
shown in Equation 1 below:

$$Br_2 + S^{2-} \rightleftharpoons 2Br^- + S \qquad\qquad \text{Equation 1}$$

25
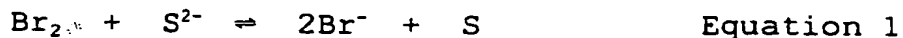
However, within an RFC such as that described in US-A-
4485154, the reaction takes place in separate but
dependent bromine and sulfur half-cell reactions as
shown below in Equations 2 and 3:

30

$$Br_2 + 2e^- \rightleftharpoons 2Br^- \qquad\qquad \text{Equation 2}$$

$$S^{2-} \rightleftharpoons 2e^- + S \qquad\qquad \text{Equation 3}$$

35   It should be noted however that these equations
represent the overall reactive changes occurring in
the RFC. In practice the reactions are complicated by

the low basicity of sulfide which results in the
formation of bisulfide as the active species, as shown
in Equation 4.

$$S^{2-} + H_2O \;\rightleftharpoons\; HS^- + OH^- \qquad \text{Equation 4}$$
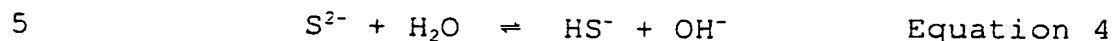
Also, the sulfur produced in Equations 1 and 3 forms
soluble polysulfide species in the presence of sulfide
ions, as shown in Equation 5 (where x may be from 1 to
4).

$$S^{2-} + xS \;\rightleftharpoons\; S_{x+1}{}^{2-} \qquad \text{Equation 5}$$

Also, free bromine is solubilised in the presence of
bromide ions to form the tribromide ion, as shown in
Equation 6

$$Br^- + Br_2 \;\rightleftharpoons\; Br_3^- \qquad \text{Equation 6}$$

When the RFC is discharging, bromine is converted to
bromide on the $+^{ve}$ side of the membrane and sulfide is
converted to polysulfide on the $-^{ve}$ side of the
membrane. Equation 1 goes from left to right and metal
ions flow from the $-^{ve}$ side of the membrane to the $+^{ve}$
side of the membrane to complete the circuit. When the
RFC is charging, bromide is converted to bromine on
the $+^{ve}$ side of the membrane and polysulfide is
converted to sulfide on the $-^{ve}$ side of the membrane.
Equation 1 goes from right to left and metal ions flow
from the $+^{ve}$ side of the membrane to the $-^{ve}$ side of
the membrane to complete the circuit.

The discharge/charge cycle described above will be
repeated many times during the lifetime of the RFC and
in order for the RFC to work efficiently throughout
its lifetime it is important that the electrolytes
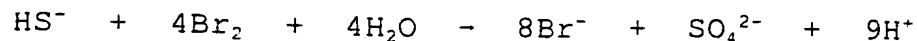remain balanced. In the context of the present

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specification, when the term "balanced" is used to
describe the electrolytes it means that the relative
concentrations of the reactive species within the
electrolytes are maintained at, or close to, values
5   which enable optimum performance of the RFC.
Similarly, in the context of the present
specification, the term "rebalancing" refers to a
process which alters the concentration of one or more
reactive species in one or both of the electrolytes so
10   as to return said electrolytes to a balanced state or
so as to maintain said electrolytes in a balanced
state.

At the beginning of the RFC's lifetime the relative
15   concentrations of the reactive species on either side
of the membrane will normally be fixed so that the
electrolytes are balanced. However, once the RFC
begins to operate in its repeating discharge-charge
cycle, factors may intervene which result in the
20   electrolytes becoming unbalanced. These factors will
vary depending upon the identity of the reactive
species within the electrolytes and on the manner in
which the RFC is constructed and operated.

25   In the case of the bromine/bromide-sulfide/polysulfide
RFC such as that described above, the most important
factor which results in the electrolytes becoming
unbalanced is the diffusion of unwanted species across
the membrane. Although a cation selective ion-
30   exchange membrane is used, 100% permselectivity is not
possible and during extended cycling of the cell some
anionic species diffuse through the membrane. In
particular, sulfide ions (largely present in the
bisulfide form, HS^-) and polysulfide ions (S_{x+1}^{2-}, where
35   x may be from 1 to 4) may diffuse from the
sulfide/polysulfide electrolyte into the
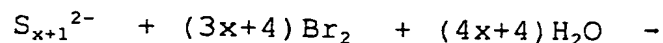bromine/bromide electrolyte where they will be

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oxidised by the bromine to form sulfate ions as shown
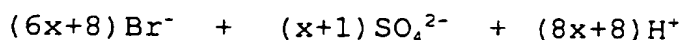in equations 7 and 8 below:

$$HS^- \ + \ 4Br_2 \ + \ 4H_2O \ - \ 8Br^- \ + \ SO_4^{2-} \ + \ 9H^+$$

5

Equation 7

$$S_{x+1}^{2-} \ + \ (3x+4)Br_2 \ + \ (4x+4)H_2O \ -$$

10
$$(6x+8)Br^- \ + \ (x+1)SO_4^{2-} \ + \ (8x+8)H^+$$

Equation 8

Imperfections other than diffusion through the
15   membrane which could similarly contribute to the above
process are ineffective sealing between cell
compartments, or catastrophic failure of any of the
cell separating components, each of which may result
in crossover of the electrolytes between cell
20   compartments.

In Equations 7 and 8, the oxidation of the sulfur
species goes beyond that which occurs during normal
operation of the RFC. That is to say, the sulfide and
25   polysulfide ions are oxidised all the way to sulfate
ions. Consequently, in the case of sulfide ion cross-
over (Equation 7), four bromine molecules per sulfide
ion are consumed rather than the normal one bromine
molecule per sulfide ion which is consumed in the
30   reaction scheme of Equation 1. Similar
overconsumption of bromine results from polysulfide
cross-over (Equation 8) although to a slightly lesser
extent. As a result, the bromine/bromide electrolyte
becomes discharged to a greater extent than the
35   sulfide/polysulfide electrolyte. Thus, when the cell
is discharging there is insufficient bromine present
to react with all the sulfide ions present thereby

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preventing completion of the discharge cycle. As a
result, the voltage generated by the cell begins to
decline earlier in the discharge cycle than when the
electrolytes are balanced. In effect, the reactions
5   represented by Equations 7 and 8 result in the
conversion of some of the polysulfide ions to sulfide
because not all of the polysulfide ions are recovered
on discharge. Subsequent cycles repeat this process,
further reducing the number of polysulfide ions
10   present. Ultimately, there will be insufficient
polysulfide ions present to accept charge during the
charge cycle. Since the electrochemistry has to
continue if charging is maintained, the next most
favourable reaction occurs, i.e. water is reduced and
15   the electrode on the $-^{ve}$ side of the cell starts to
gas hydrogen.

It would therefore be advantageous to provide a
process for rebalancing the electrolytes in order to
20   compensate for the unbalancing effect of the crossover
of sulfide and/or polysulfide electrolyte species into
the bromine electrolyte. Although it would be
possible to replace the electrolytes in the system
with fresh electrolytes at periodic intervals, this is
25   disadvantageous because of the economic implications
and because of the environmental implications of the
great amounts of waste electrolytes which would
require to be disposed of.

30   Accordingly, the present invention provides an
electrochemical process for energy storage and/or
power delivery comprising:
       (i)   maintaining and circulating electrolyte flows in
             a fully liquid system in which the active
35   constituents are fully soluble in a single cell
             or in an array of repeating cell structures, each
             cell with a positive ($+^{ve}$) chamber containing an

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inert $+^{ve}$ electrode and a negative ($-^{ve}$) chamber
containing an inert $-^{ve}$ electrode, the chambers
being separated from one another by a cation
exchange membrane, the electrolyte circulating in
5   the $-^{ve}$ chamber of each cell during power
delivery containing a sulfide (electrolyte 1),
and the electrolyte circulating in the $+^{ve}$
chamber during power delivery containing bromine
(electrolyte 2),

10   (ii) restoring or replenishing the electrolytes in the
$+^{ve}$ and $-^{ve}$ chambers by circulating the
electrolyte from each chamber to storage means
comprising a volume of electrolyte greater than
the cell volume for extended delivery of power
15   over a longer discharge cycle than the cell
volume alone would permit, and

(iii) rebalancing the electrolytes by circulating a
fraction of electrolyte 1 or electrolyte 2
through the $+^{ve}$ chamber of an auxiliary cell,
20   said auxiliary cell comprising a $+^{ve}$ chamber
containing an inert $+^{ve}$ electrode and a $-^{ve}$
chamber containing an inert $-^{ve}$ electrode, the
chambers being separated from one another by a
cation exchange membrane, the electrolyte
25   circulating through the $-^{ve}$ chamber of the
auxiliary cell containing water and being free
from polysulfide and free from bromine during
rebalancing, the auxiliary cell operating so as
to oxidise sulfide ions to sulfur or bromide ions
30   to bromine in the $+^{ve}$ chamber and so as to reduce
water to hydrogen and hydroxide ions in the $-^{ve}$
chamber.

The oxidation of bromide to bromine rebalances the
35   electrolytes by restoring the bromine which is reduced
by reaction with migrating sulfide ions. Oxidation of
bromide to bromine may also be thought of as charging

the bromine/bromide electrolyte since the chemical
content of the bromine/bromide electrolyte changes in
the same manner as when the RFC is in its charging
cycle.

5

The oxidation of sulfide to sulfur rebalances the
electrolytes by oxidising the equivalent amount of
sulfide which would ordinarily have been oxidised by
the halogen which was reduced by reaction with
10   migrating sulfide ions. Oxidation of polysulfide to
sulfur may also be thought of as discharging the
sulfide/polysulfide electrolyte since the chemical
content of the sulfide/polysulfide electrolyte changes
in the same manner as in the RFC when it is in its
15   discharging cycle.

In order that rebalancing of the electrolytes may
occur, it is essential that during the rebalancing
process the electrolyte circulating through the $-^{ve}$
20   chamber of the auxiliary cell should be free from
polysulfide and free from bromine. The reason for this
is that these chemical species are more readily
reduced than water. If electrolyte 1 is circulated
through the $+^{ve}$ chamber of the auxiliary cell and the
25   electrolyte circulating through the $-^{ve}$ chamber of the
auxiliary cell contains polysulfide, then the reaction
which will occur in the $-^{ve}$ chamber will be reduction
of polysulfide to sulfide rather than reduction of
water to hydrogen and hydroxide ions. This would
30   result in no net change in the oxidation state of the
sulfur species present in the system. If reduction of
water is to occur in the presence of polysulfide the
$-^{ve}$ electrode in the $-^{ve}$ chamber must be specially
constructed to starve it of polysulfide. Similarly, if
35   electrolyte 2 is circulated through the $+^{ve}$ chamber of
the auxiliary cell and the electrolyte circulating
through the $-^{ve}$ chamber of the auxiliary cell contains

bromine, then the reaction which will occur in the $-^{ve}$ chamber will be reduction of bromine to bromide rather than reduction of water to hydrogen and hydroxide ions. This would result in no net change in the
5   oxidation state of the bromine species present in the system. If reduction of water is to occur in the presence of bromine the $-^{ve}$ electrode in the $-^{ve}$ chamber must be specially constructed to starve it of bromine. Inclusion of such specially constructed
10   electrodes is clearly undesirable from an economic and system maintenance viewpoint.
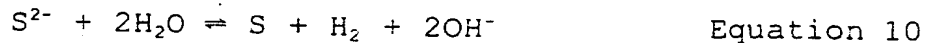
The rebalancing process may be applied continuously to the RFC wherein a sidestream of the bromine/bromide or
15   sulfide/polysulfide electrolyte drawn from the mainstream is diverted through apparatus suitable for carrying out the rebalancing process. The rebalancing process may also be applied as a batch process wherein the fraction of the bromine/bromide or
20   sulfide/polysulfide electrolyte which is removed from the RFC is treated in separate apparatus suitable for carrying out the rebalancing process before being returned to the RFC.

25   It will be understood by those skilled in the art that a number of reduction half-cell reactions may be used to counter the oxidation of the halide or sulfide. However, in the present invention, the other half-cell reaction under alkaline conditions involves the
30   reduction of water to hydrogen and hydroxide ions according to the half-cell reaction shown in Equation 8 below:

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad \text{Equation 8}$$

35
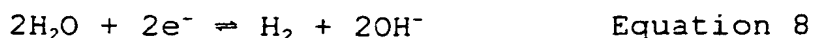
Thus the rebalancing process may be represented by the reactions shown in Equations 9 and 10 below:

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$$2Br^- + 2H_2O \rightleftharpoons Br_2 + H_2 + 2OH^- \qquad \text{Equation 9}$$

$$S^{2-} + 2H_2O \rightleftharpoons S + H_2 + 2OH^- \qquad \text{Equation 10}$$

Similarly in an acidic medium the half cell reaction comprises

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad \text{Equation 11}$$

It will be appreciated that, although the process of oxidising the bromine/bromide or sulfide/polysulfide electrolyte can be used to rebalance the electrolytes, there is still a net loss of active sulfur species from the cell. This is because the sulfide and polysulfide ions which cross to the bromine electrolyte and are oxidised to sulfate ions are not recovered. Thus, in a preferred embodiment of the present invention, the process additionally comprises adding elemental sulfur or a sulfide salt to the sulfide/polysulfide electrolyte in an amount such as to restore the initial concentration of active sulfur species.

In carrying out the process of the present invention the electrolyte circulating through the $-^{ve}$ chamber of the auxiliary cell may be water. In this instance the electrolyte will generally circulate in a closed system and there will be no change of pH of the bromine/bromide or sulfide/polysulfide electrolyte.

In an alternative manner of carrying out the process of the present invention the electrolyte circulating through the $-^{ve}$ chamber of the auxiliary cell is a fraction of electrolyte 1 or 2 which has been made free of polysulfide or bromine by electrochemical reduction thereof. This may be achieved by recirculating electrolyte 1 or 2 through the $-^{ve}$

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chamber of the auxiliary cell until all of the
polysulfide or bromine has been reduced. The
electrolyte circulating through the $-^{ve}$ chamber of the
auxiliary cell may then be returned to the main stream
5   of electrolyte 1 or 2.

Alternatively, the electrochemical reduction of
polysulfide or bromine which may be present in
electrolyte 1 or 2 respectively occurs within the $-^{ve}$
10   chamber of a second auxiliary cell which comprises a
$+^{ve}$ chamber containing an inert $+^{ve}$ electrode and a $-^{ve}$
chamber containing an inert $-^{ve}$ electrode, the
chambers being separated from one another by a cation
exchange membrane, the electrolyte circulating through
15   the $+^{ve}$ chamber being a fraction of electrolyte 1 or
electrolyte 2. This may be achieved by recirculating
electrolyte 1 or 2 through the $-^{ve}$ chamber of the
second auxiliary cell until all of the polysulfide or
bromine has been reduced. The electrolyte circulating
20   through the $-^{ve}$ chamber of the auxiliary cell may then
be returned to the main stream of electrolyte 1 or 2.

Another reason why the reduction of any bromine which
may be present in electrolyte 2 is important is
25   because, as described in WO-A-00/03448, carrying out
the RFC process of the present invention results in
the production of sulfate ions in the bromine/bromide
electrolyte as described above with reference to
Equation 7. The removal of sulfate ions from the
30   electrolyte can only be carried out by the process as
described in WO-A-00/03448 in the absence of free
bromine which otherwise interferes with the process.
Thus, in a preferred embodiment, the electrolyte
circulating through the $-^{ve}$ chamber of the auxiliary
35   cell during rebalancing is a fraction of electrolyte 2
and that fraction is subsequently treated to remove
sulfate ions contained therein.

In carrying out the process of the present invention
elemental sulfur and/or a sulfide salt may be added to
the sulfide/polysulfide electrolyte in an amount
sufficient to restore the initial concentration of
5   sulfur species.

The present invention also provides for the use, in a
process for energy storage and/or power delivery
comprising:

10   (i)   maintaining and circulating electrolyte flows in
           a fully liquid system in which the active
           constituents are fully soluble in a single cell
           or in an array of repeating cell structures, each
           cell with a positive ($+^{ve}$) chamber containing an
15   inert $+^{ve}$ electrode and a negative ($-^{ve}$) chamber
           containing an inert $-^{ve}$ electrode, the chambers
           being separated from one another by a cation
           exchange membrane, the electrolyte circulating in
           the $-^{ve}$ chamber of each cell during power
20   delivery containing a sulfide (electrolyte 1),
           and the electrolyte circulating in the $+^{ve}$
           chamber during power delivery containing bromine
           (electrolyte 2),

      (ii) restoring or replenishing the electrolytes in the
25         $+^{ve}$ and $-^{ve}$ chambers by circulating the
           electrolyte from each chamber to storage means
           comprising a volume of electrolyte greater than
           the cell volume for extended delivery of power
           over a longer discharge cycle than the cell
30   volume alone would permit,

      of a process comprising:
           circulating a fraction of electrolyte 1 or
           electrolyte 2 through the $+^{ve}$ chamber of an
           auxiliary cell, said auxiliary cell comprising a
35         $+^{ve}$ chamber containing an inert $+^{ve}$ electrode and
           a $-^{ve}$ chamber containing an inert $-^{ve}$ electrode,
           the chambers being separated from one another by

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a cation exchange membrane, the electrolyte
circulating through the $-^{ve}$ chamber of the
auxiliary cell containing water and being free
from polysulfide and free from bromine during
5   rebalancing, the auxiliary cell operating so as
to oxidise sulfide ions to polysulfide or bromide
ions to bromine in the $+^{ve}$ chamber and so as to
reduce water to hydrogen and hydroxide ions in
the $-^{ve}$ chamber,
10   for the purpose of rebalancing electrolytes 1 and 2.

The present invention also includes within its scope
apparatus for carrying out a process as described
above comprising:
15   (i)   a single cell or an array of repeating cell
structures, each cell comprising; a $+^{ve}$ chamber
containing an inert $+^{ve}$ electrode and a $-^{ve}$
chamber containing an inert $-^{ve}$ electrode the
chambers being separated from one another by an
20   ion exchange membrane, an electrolyte circulating
in the $-^{ve}$ chamber of each cell which contains a
sulfide during power delivery (electrolyte 1),
and an electrolyte circulating in the $+^{ve}$ chamber
which contains bromine during power delivery
25   (electrolyte 2),
(ii) storage and circulation means for each
electrolyte for restoring or replenishing the
electrolytes in the $+^{ve}$ and $-^{ve}$ chambers,
(iii) means for rebalancing the electrolytes
30   comprising an auxiliary cell which comprises a
$+^{ve}$ chamber containing an inert $+^{ve}$ electrode and
a $-^{ve}$ chamber containing an inert $-^{ve}$ electrode
the chambers being separated from one another by
a cation exchange membrane, means for circulating
35   a fraction of electrolyte 1 or 2 through the $+^{ve}$
chamber of the auxiliary cell, an electrolyte
containing water and being free from polysulfide

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and free from bromine during rebalancing and
means for circulating said electrolyte through
the -^{ve} chamber of the auxiliary cell.

5   The present invention will be further described with
reference to the accompanying drawings in which:

Fig 1A is a schematic view of a basic electrochemical
reduction-oxidation cell in which a
10   sulfide/polysulfide reaction is carried out in one
half of the cell and a bromine/bromide reaction is
carried out in the other half of the cell;

Fig 1B is a diagram of cell arrays using the system of
15   Fig 1A;

Fig 2 is a block diagram of a fluid flow system using
the cell of Fig 1A;

20   Fig 3 is a flow diagram of an apparatus for carrying
out a preferred embodiment of the process of the
present invention.

Fig 4 is a flow diagram of an apparatus for carrying
25   out a preferred embodiment of the process of the
present invention.

Fig 5 is a schematic diagram of an apparatus for
carrying out a further preferred embodiment of the
30   process of the present invention, including the
removal of sulfate.

Fig 6 is a flow diagram of an apparatus for carrying
out a preferred embodiment of the process of the
35   present invention, including the removal of sulfate.

Fig 7 is a graph of voltage versus time for a selected

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number of cycles of a RFC which does not incorporate a rebalancing process in accordance with the present invention.

5   Fig 8 is a graph of voltage versus time for a selected number of cycles of a RFC which does incorporate a rebalancing process in accordance with the present invention.

10   Fig 1A shows a cell 10 with a positive (+^{ve}) electrode 12 and a negative (-^{ve}) electrode 14 and a cation exchange membrane 16 which may be formed from a fluorocarbon polymer with sulfonic acid functional groups to provide charge carriers. The membrane 16
15   acts to separate the +^{ve} and -^{ve} sides of the cell 10 and is selected to minimize migration of bromine from the +^{ve} side to the -^{ve} side and to minimize migration of sulfide and polysulfide ions from the -^{ve} side to the +^{ve} side. An aqueous solution 22 of NaBr is
20   provided in a chamber 22C formed between the +^{ve} electrode 12 and the membrane 16 and an aqueous solution 24 of Na_2S_x (where x may be from 2 to 5) is provided in a chamber 24C formed between the -^{ve} electrode 14 and the membrane 16. A K_2S_x solution,
25   which is more soluble and more expensive than the Na_2S_x solutions, is used in another embodiment.

When the cell is in the discharged state, a solution of NaBr of up to 6.0 molar concentration
30   exists in the chamber 22C of the cell and a solution of Na_2S_x at 0.5 to 1.5 molar, exists in chamber 24C of the cell. Higher molarity is possible with K_2S_x.

As the cell is charged, Na$^+$ ions are transported
35   through the cation membrane 16, as shown in Fig 1A, from the +^{ve} to the -^{ve} side of the cell. Free bromine is produced via oxidation of the bromide ions at the
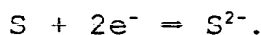
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+^{ve} electrode and dissolves as a tribromide or
pentabromide ion. Sulfur is reduced at the -^{ve}
electrode and the pentasulfide, Na_2S_x, salt eventually
becomes the monosulfide as the charging proceeds to
5   completion. At the +^{ve} side the following reaction
occurs,

$$2Br^- \rightleftharpoons Br_2 + 2e^-$$
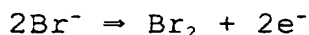
10   and at the -^{ve} side the following reaction occurs,

$$S + 2e^- \rightleftharpoons S^{2-}.$$

The membrane separates the two electrolytes and
15   prevents bulk mixing and also retards the migration of
sulfide and polysulfide ions from the -^{ve} side to the
+^{ve} side, and the migration of Br$^-$ and Br_2 from the +^{ve}
to the -^{ve} side. Diffusion of the sulfide and
polysulfide ions across the membrane results in the
20   electrolytes becoming unbalanced as described earlier.

When providing power, the cell is discharging. During
this action, reversible reactions occur at the two
electrodes. At the +^{ve} side electrode 12, bromine is
25   reduced to Br$^-$, and at the -^{ve} electrode, the S^{2-} ion is
oxidized to molecular S. The electrons produced at the
-^{ve} electrode form the current through a load. The
chemical reaction at the +^{ve} electrode produces 1.06
to 1.09 volts and the chemical reaction at the -^{ve}
30   electrode produces 0.48 to 0.52 volts. The combined
chemical reactions produce an open circuit voltage of
1.54 to 1.61 volts per cell.

The present system is an anionically active
35   electrochemical system. Therefore, the cation which is
associated with them essentially takes no part in the
energy producing process. Hence, a cation of

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"convenience" is chosen. Sodium or potassium are
preferred choices. Sodium and potassium compounds are
plentiful, they are inexpensive and have high water
solubilities. Lithium and ammonium salts are also
5   possibilities, but at higher costs.

Fig 1B shows an array 20 of multiple cells connected
in electrical series and fluid parallel. Multiple mid-
electrodes 13 (each one having a $+^{ve}$ electrode side
10   12A and $-^{ve}$ electrode side 14A) and end electrodes 12E
($+^{ve}$) and 14E ($-^{ve}$) are spaced out from each other by
membranes 16 and screen or mesh spacers (22D, 24D) in
all the cell chambers 22C, 24C, (portions of two of
which 22D, 24D are shown by way of example) to form
15   end cells C_{E1} and C_{E2} and an array of mid cells C_M
(typically 10-20; but note much smaller and much
higher numbers of cells can be accommodated). The end
electrodes 12E ($+^{ve}$) and 14E ($-^{ve}$) have internal
conductors 12F and 14F (typically copper screens)
20   encapsulated therein and leading to external terminals
12G, 14G which are connected to external loads (e.g.
to motor(s) via a control circuit (CONT), the motor(s)
may be used to drive a vehicle) or power sources (e.g.
utility power grid when used as a load-levelling
25   device).

Fig 2 shows a free flow system, a power
generation/storage system utilizing one or more of the
batteries or cell array formats 20. Each cell 20
30   receives electrolyte through pumps 26 and 28 for the
NaBr and Na_2S_x solutions (22 and 24, respectively).
The electrolytes 22 and 24 are stored in containers 32
and 34. The tanks 32, 34 can be replaced with freshly
charged electrolyte by substituting tanks containing
35   fresh electrolyte and/or refilling them from charged
supply sources via lines 32R, 34R with corresponding
lines (not shown) provided for draining spent

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(discharged) reagent. The electrolytes 22 and 24 are pumped from tanks 32 and 34, respectively, into the respective chambers 22C and 24C by means of pumps 26 and 28.

5

Fig 3 shows a free flow system in which an array of cells 20 are supplied with bromine/bromide and sulfide/polysulfide electrolyte from storage tanks 41 and 42 via lines 43 and 44. Bromine/bromide

10 electrolyte may be removed from storage tank 41 via line 50 which transfers it to an external electrochemical cell 51 wherein the bromide is oxidised to bromine as a half-cell reaction in an electrochemical process. The other half-cell reaction

15 involves the reduction of water to hydrogen and hydroxide ions. An aqueous electrolyte is stored in tank 52 and transported to the electrochemical cell 51 via line 53. The reduced electrolyte is passed via line 54 to tank 55 where hydrogen gas which is

20 generated by the electrochemical reaction may be vented from the system. The electrolyte returns via line 56 to storage tank 52.

Fig 4 shows a particularly preferred variation of the

25 free flow system illustrated in Fig 3. In this embodiment the aqueous electrolyte which is reduced in the external electrochemical cell 51 is also bromine/bromide electrolyte which has been removed from storage tank 41 to tank 52 via line 57. In this

30 case, the reduction reaction will initially involve reduction of any residual bromine to bromide and will subsequently involve reduction of water to hydrogen and hydroxide ions. The reduced electrolyte may be subsequently returned to the storage tank 41 along

35 line 58.

Referring to Fig 5, a schematic flow diagram is shown

- 18 -

of the manner in which the electrolyte may be treated.
A storage tank 41 contains the aqueous bromine/bromide
electrolyte which may be circulated around the main
RFC system (not shown). The first treatment of a
5   first stream of the electrolyte from tank 41 is to
remove free bromine by treatment in an appropriate
bromine reduction module 61 which comprises an
auxiliary cell. The electrolyte is circulated via
module 61 and an intermediate storage tank 62 until
10   the bromine present in the electrolyte is reduced to
bromide. When the reduction is complete the
electrolyte is passed to storage tank 63. A second
stream of the electrolyte from tank 41 is passed to an
electrochemical cell module 64 where the bromide is
15   oxidised to bromine as a half-cell reaction in an
electrochemical process. The other half-cell reaction
involves the reduction of water to hydrogen and
hydroxyl ions using as the electrolyte for the
hydroxyl ion production the electrolyte from storage
20   tank 63. The stream of electrolyte passing through
module 64 in which bromide has been oxidised to
bromide is returned to the storage tank 41. The
stream of electrolyte used in the complementary half-
cell reaction may be passed to a further tank 65 where
25   it is then subjected to a sulfate removal treatment
according to the teaching of WO-A-00/03448 in module
66. The stream of electrolyte from which the sulfate
has been removed is then returned to the original
storage tank 41. Storage tank 63 is provided with
30   appropriate means to vent hydrogen produced in the
water reduction reaction to a hydrogen stack along
line 67.

Fig 6 shows an alternative system for use in
35   accordance with the present invention which includes a
sulfate crystallization unit as described in WO-A-
00/03448. In this system a portion of bromide/bromine

electrolyte contaminated with sulfate ions is drawn
from the main system 80 via line 81 and held in a
receiving tank 82. This electrolyte is then
circulated via lines 83 and 84 through the $-^{ve}$ chamber
5   85 of an auxiliary cell 86 until substantially all of
the bromine present in the electrolyte has been
reduced to bromide ions. The voltage applied across
cell 86 is limited to ensure that reduction of water
does not occur. When the current density has run down
10   (thus indicating that the conversion of bromine to
bromide is substantially complete), the voltage
applied to the cell 86 is increased to a value
sufficient to cause reduction of the water present in
the electrolyte so as to generate H_2 gas and OH^- ions.
15   The electrolyte circulating through the $+^{ve}$ chamber of
the external auxiliary cell is either
sulfide/polysulfide or bromine/bromide electrolyte
taken from the main system. The oxidation of one or
the other of these electrolytes rebalances the system.
20   The removal of water from the electrolyte is
advantageous because it further increases the
concentration of bromide ions thereby reducing the
sulfate solubility and increasing the yield of sulfate
on crystallisation. A tap 87 is provided to draw off
25   H_2 gas. When sufficient rebalancing has occurred, the
electrolyte circulating through the $-^{ve}$ chamber 85 is
passed from the receiving tank 82 to the crystalliser
88 via line 89. This electrolyte is then passed via
line 90 through a filter 91 to remove the sulfate
30   crystals and then it may be returned to the main
system via line 92. The embodiment shown in Fig 6
shows an electrolyte being drawn from the main system
via line 93, passing through the $+^{ve}$ chamber 94 of the
auxiliary cell and returning the main system via line
35   95.

The present invention will now be further described by

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reference to the following examples.

Comparative Example 1

A regenerative fuel cell of the type described above
having sulfide/polysulfide and bromine/bromide
electrolytes was set up. The cell had the following
specifications:

electrode material: polyethylene impregnated with
                    activated carbon
electrode area: 2000cm²
current density: 80mA/cm²
electrolyte volume: 9l per electrolyte
cycle time: 6hours (i.e. 3hours charge
                    and 3hours discharge)
flow rate: 1000ml/min
membrane material: Nafion 115™

The cell was operated over 18 cycles (108 hours) and
the cell voltage was monitored throughout this period.
The results are shown in Fig 7. It can be seen that
after a limited number of cycles (about 7) the cell
voltage limits early on the discharge cycle due to the
lack of bromine. This problem gets worse as the
number of cycles increases. It can be clearly seen on
the graph that after about 12 cycles (72 hours) the
cell fails to maintain a good voltage performance over
the whole of the 3 hour discharge cycle.

Example 1

An identical RFC to that used in Comparative Example 1
was set up. This time the electrolytes were
continuously rebalanced by oxidation of a sidestream
of the bromide/bromine electrolyte drawn from the
mainstream. Oxidation occurred in one half of an
external electrochemical cell wherein the electrolyte

undergoing reduction in the other half of the cell was
dilute aqueous sodium hydroxide. The external
electrochemical cell used was an MP cell from
Electrocell AB having the following specifications:

5

anode material:	platinum
cathode material:	nickel
electrode area:	$100cm^2$
current density:	$13mA/cm^2$
flow rate:	270ml/min
membrane material:	Nafion 350™

10

Fig.3 shows a schematic representation of the
apparatus used in the present example. The cell was
15 operated over at least 92 cycles (552 hours) and the
cell voltage was monitored throughout this period. The
results from the period from 400 to 550 hours are
shown in Fig 8. It can be seen that even after 91
cycles (546 hours) the cell voltage does not limit
20 early on the discharge cycle as occurred in the
unbalanced cell. The cell retains a good voltage
performance over the whole of the 3 hour discharge
cycle.

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CLAIMS:

1. An electrochemical process for energy storage
and/or power delivery comprising:

5   (i)   maintaining and circulating electrolyte flows in
            a fully liquid system in which the active
            constituents are fully soluble in a single cell
            or in an array of repeating cell structures, each
            cell with a positive ($+^{ve}$) chamber containing an

10   inert $+^{ve}$ electrode and a negative ($-^{ve}$) chamber
            containing an inert $-^{ve}$ electrode, the chambers
            being separated from one another by a cation
            exchange membrane, the electrolyte circulating in
            the $-^{ve}$ chamber of each cell during power

15   delivery containing a sulfide (electrolyte 1),
            and the electrolyte circulating in the $+^{ve}$
            chamber during power delivery containing bromine
            (electrolyte 2),

      (ii) restoring or replenishing the electrolytes in the
20          $+^{ve}$ and $-^{ve}$ chambers by circulating the
            electrolyte from each chamber to storage means
            comprising a volume of electrolyte greater than
            the cell volume for extended delivery of power
            over a longer discharge cycle than the cell

25   volume alone would permit, and

      (iii) rebalancing the electrolytes by circulating a
            fraction of electrolyte 1 or electrolyte 2
            through the $+^{ve}$ chamber of an auxiliary cell,
            said auxiliary cell comprising a $+^{ve}$ chamber

30   containing an inert $+^{ve}$ electrode and a $-^{ve}$
            chamber containing an inert $-^{ve}$ electrode, the
            chambers being separated from one another by a
            cation exchange membrane, the electrolyte
            circulating through the $-^{ve}$ chamber of the

35   auxiliary cell containing water and being free
            from polysulfide and free from bromine during
            rebalancing, the auxiliary cell operating so as

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to oxidise sulfide ions to sulfur or bromide ions to bromine in the $+^{ve}$ chamber and so as to reduce water to hydrogen and hydroxide ions in the $-^{ve}$ chamber.

2.   A process as claimed in claim 1 wherein the electrolyte circulating through the $-^{ve}$ chamber of the auxiliary cell during rebalancing is a fraction of electrolyte 1 or electrolyte 2 which has been made free of polysulfide or bromine by electrochemical reduction thereof.

3.   A process as claimed in claim 2 wherein the electrochemical reduction of polysulfide or bromine is effected by recirculating the fraction of electrolyte 1 or 2 through the $-^{ve}$ chamber of the auxiliary cell until all of the polysulfide or bromine has been reduced.

4.   A process as claimed in claim 2 wherein the electrochemical reduction of polysulfide or bromine occurs within the $-^{ve}$ chamber of a second auxiliary cell which comprises a $+^{ve}$ chamber containing an inert $+^{ve}$ electrode and a $-^{ve}$ chamber containing an inert $-^{ve}$ electrode, the chambers being separated from one another by a cation exchange membrane, the electrolyte circulating through the $+^{ve}$ chamber being a fraction of electrolyte 1 or electrolyte 2.

5.   A process as claimed in claim 4 wherein the electrochemical reduction of polysulfide or bromine is effected by recirculating the fraction of electrolyte 1 or 2 through the $-^{ve}$ chamber of the second auxiliary cell until all of the polysulfide or bromine has been reduced.

6.   A process as claimed in any one of claims 3 to 5

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wherein the electrolyte circulating through the -^{ve}
chamber of the auxiliary cell during rebalancing is a
fraction of electrolyte 2 and wherein that fraction is
subsequently treated to remove sulfate ions contained

5   therein.

7.   A process as claimed in claim 6 wherein said
sulfate ions are removed by crystallisation of a
sulfate salt from the fraction of electrolyte 2.

10

8.   A process as claimed in any one of claims 2 to 7
wherein the fraction of electrolyte 1 or 2 which is
circulated through the -^{ve} chamber of the auxiliary
cell is returned to the main stream of electrolyte 1

15   or 2 respectively.

9.   A process as claimed in any one of the preceding
claims which additionally comprises adding elemental
sulfur and/or a sulfide salt to electrolyte 1 in an

20   amount sufficient to restore the initial concentration
of sulfur species.

10.   Use, in a process for energy storage and/or power
delivery comprising:

25   (i)   maintaining and circulating electrolyte flows in
          a fully liquid system in which the active
          constituents are fully soluble in a single cell
          or in an array of repeating cell structures, each
          cell with a positive (+^{ve}) chamber containing an

30   inert +^{ve} electrode and a negative (-^{ve}) chamber
          containing an inert -^{ve} electrode, the chambers
          being separated from one another by a cation
          exchange membrane, the electrolyte circulating in
          the -^{ve} chamber of each cell during power

35   delivery containing a sulfide (electrolyte 1),
          and the electrolyte circulating in the +^{ve}
          chamber during power delivery containing bromine

(electrolyte 2),

(ii) restoring or replenishing the electrolytes in the $+^{ve}$ and $-^{ve}$ chambers by circulating the electrolyte from each chamber to storage means

5   comprising a volume of electrolyte greater than the cell volume for extended delivery of power over a longer discharge cycle than the cell volume alone would permit,

of a process comprising:

10   circulating a fraction of electrolyte 1 or electrolyte 2 through the $+^{ve}$ chamber of an auxiliary cell, said auxiliary cell comprising a $+^{ve}$ chamber containing an inert $+^{ve}$ electrode and a $-^{ve}$ chamber containing an inert $-^{ve}$ electrode,

15   the chambers being separated from one another by a cation exchange membrane, the electrolyte circulating through the $-^{ve}$ chamber of the auxiliary cell containing water and being free from polysulfide and free from bromine during

20   rebalancing, the auxiliary cell operating so as to oxidise sulfide ions to polysulfide or bromide ions to bromine in the $+^{ve}$ chamber and so as to reduce water to hydrogen and hydroxide ions in the $-^{ve}$ chamber,

25 for the purpose of rebalancing electrolytes 1 and 2.

11. An electrochemical apparatus for energy storage and/or power delivery comprising:

(i) a single cell or an array of repeating cell

30   structures, each cell comprising; a $+^{ve}$ chamber containing an inert $+^{ve}$ electrode and a $-^{ve}$ chamber containing an inert $-^{ve}$ electrode the chambers being separated from one another by an ion exchange membrane, an electrolyte circulating

35   in the $-^{ve}$ chamber of each cell which contains a sulfide during power delivery (electrolyte 1), and an electrolyte circulating in the $+^{ve}$ chamber

which contains bromine during power delivery
(electrolyte 2),

(ii) storage and circulation means for each
electrolyte for restoring or replenishing the
electrolytes in the $+^{ve}$ and $-^{ve}$ chambers,

(iii) means for rebalancing the electrolytes
comprising an auxiliary cell which comprises a
$+^{ve}$ chamber containing an inert $+^{ve}$ electrode and
a $-^{ve}$ chamber containing an inert $-^{ve}$ electrode
the chambers being separated from one another by
a cation exchange membrane, means for circulating
a fraction of electrolyte 1 or 2 through the $+^{ve}$
chamber of the auxiliary cell, an electrolyte
containing water and being free from polysulfide
and free from bromine during rebalancing and
means for circulating said electrolyte through
the $-^{ve}$ chamber of the auxiliary cell.

12.   Apparatus as claimed in claim 11 wherein the
means for circulating an electrolyte through the $-^{ve}$
chamber of the auxiliary cell comprises means for
circulating a fraction of electrolyte 1 or 2 through
the $-^{ve}$ chamber of the auxiliary cell.

13.   Apparatus as claimed in claim 11 wherein the
means for circulating an electrolyte through the $-^{ve}$
chamber of the auxiliary cell comprises a storage tank
into which a fraction of electrolyte 1 or 2 may be
transferred and means for re-circulating the fraction
of electrolyte 1 or 2 between the $-^{ve}$ chamber of the
auxiliary cell and said storage tank.

14.   Apparatus as claimed in claim 12 or claim 13
which additionally comprises a second auxiliary cell
which comprises a $+^{ve}$ chamber containing an inert $+^{ve}$
electrode and a $-^{ve}$ chamber containing an inert $-^{ve}$
electrode, the chambers being separated from one

another by a cation exchange membrane, means for
circulating a fraction of electrolyte 1 or 2 through
the +^{ve} chamber and means for circulating a fraction
of electrolyte 1 or 2 through the -^{ve} chamber.

5

15.   Apparatus as claimed in claim 14 wherein the
means for circulating an electrolyte through the -^{ve}
chamber of the second auxiliary cell comprises a
storage tank into which a fraction of electrolyte 1 or
10   2 may be transferred and means for re-circulating the
fraction of electrolyte 1 or 2 between the -^{ve} chamber
of the second auxiliary cell and said storage tank.

16.   Apparatus as claimed in any one of claims 12 to
15   15 wherein the electrolyte circulated through the -^{ve}
chamber of the auxiliary cell is electrolyte 2,
additionally comprising means for removing sulfate
ions from the fraction of electrolyte 2 after
circulation through the -^{ve} chamber of the auxiliary
20   cell.

17.   Apparatus as claimed in claim 16 wherein the
means for removing sulfate ions from electrolyte 2
comprises a crystalliser.

25

18.   Apparatus as claimed in any one of claims 11 to
17 additionally comprising means for passing the
fraction of electrolyte 1 or 2 which is circulated
through the -^{ve} chamber of the auxiliary cell back to
30   the main stream of electrolyte 1 or 2 respectively.

19.   Use in an electrochemical apparatus for energy
storage and/or power delivery comprising:
(i)   a single cell or an array of repeating cell
35   structures, each cell comprising; a +^{ve} chamber
containing an inert +^{ve} electrode and a -^{ve}
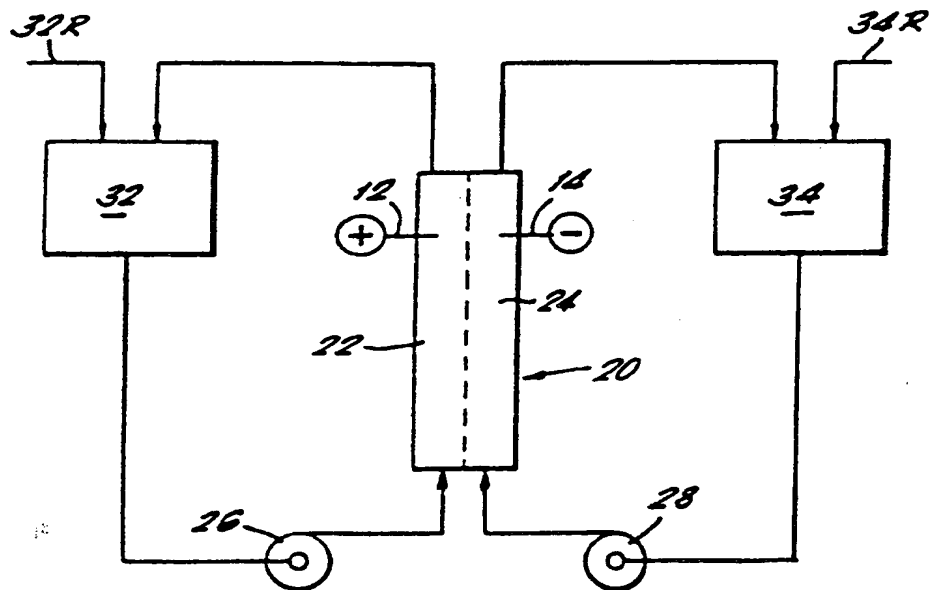chamber containing an inert -^{ve} electrode the

chambers being separated from one another by an
ion exchange membrane, an electrolyte circulating
in the $-^{ve}$ chamber of each cell which contains a
sulfide during power delivery (electrolyte 1),

5   and an electrolyte circulating in the $+^{ve}$ chamber
which contains bromine during power delivery
(electrolyte 2), and

(ii) storage and circulation means for each
electrolyte for restoring or replenishing the

10   electrolytes in the $+^{ve}$ and $-^{ve}$ chambers,

of

an auxiliary cell which comprises; a $+^{ve}$ chamber
containing an inert $+^{ve}$ electrode and a $-^{ve}$
chamber containing an inert $-^{ve}$ electrode the

15   chambers being separated from one another by a
cation exchange membrane, means for passing a
fraction of electrolyte 1 or 2 through the $+^{ve}$
chamber of the auxiliary cell, an electrolyte
containing water and being free from polysulfide

20   and free from bromine during rebalancing and
means for circulating said electrolyte through
the $-^{ve}$ chamber of the auxiliary cell

for the purpose of rebalancing electrolytes 1 and 2.
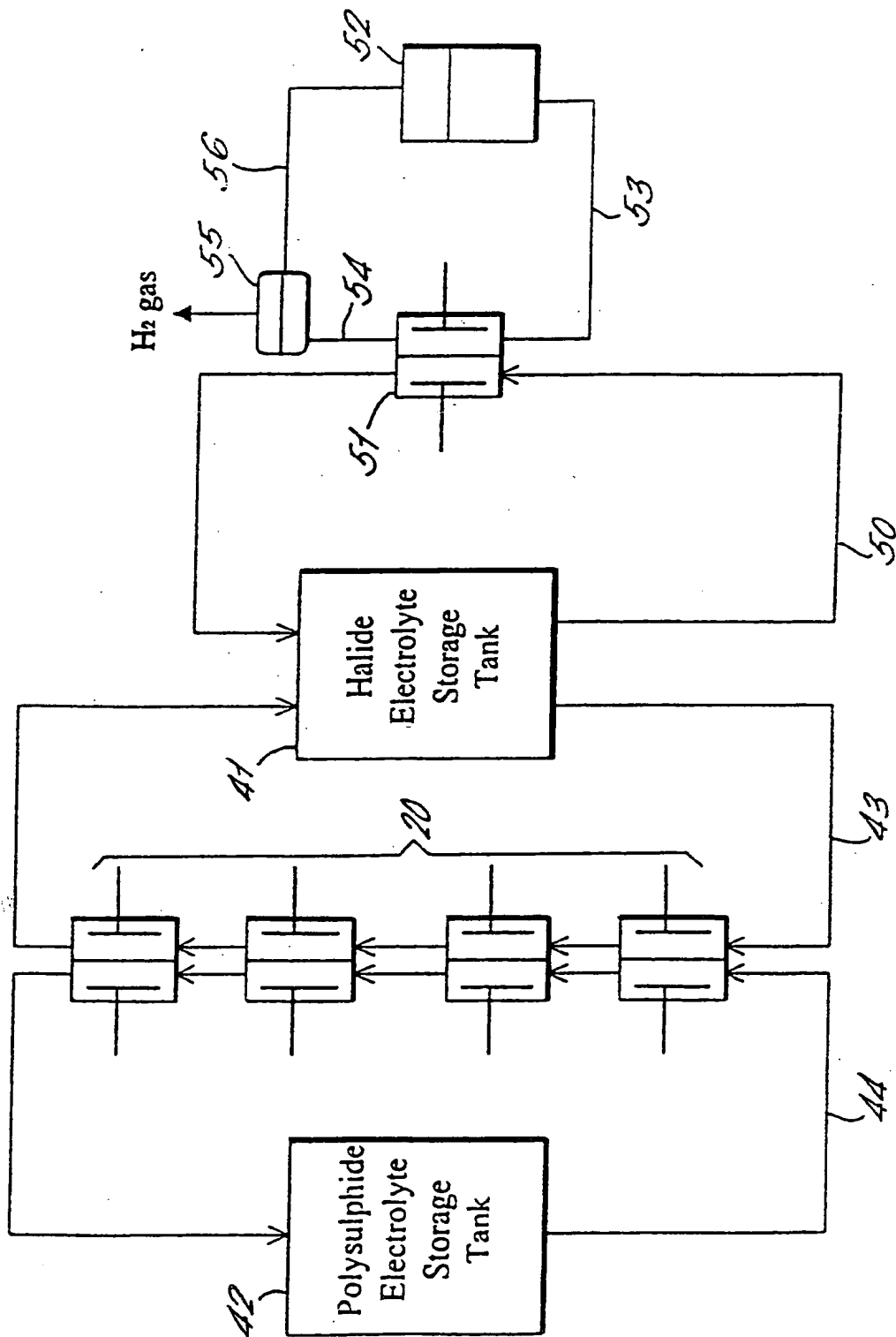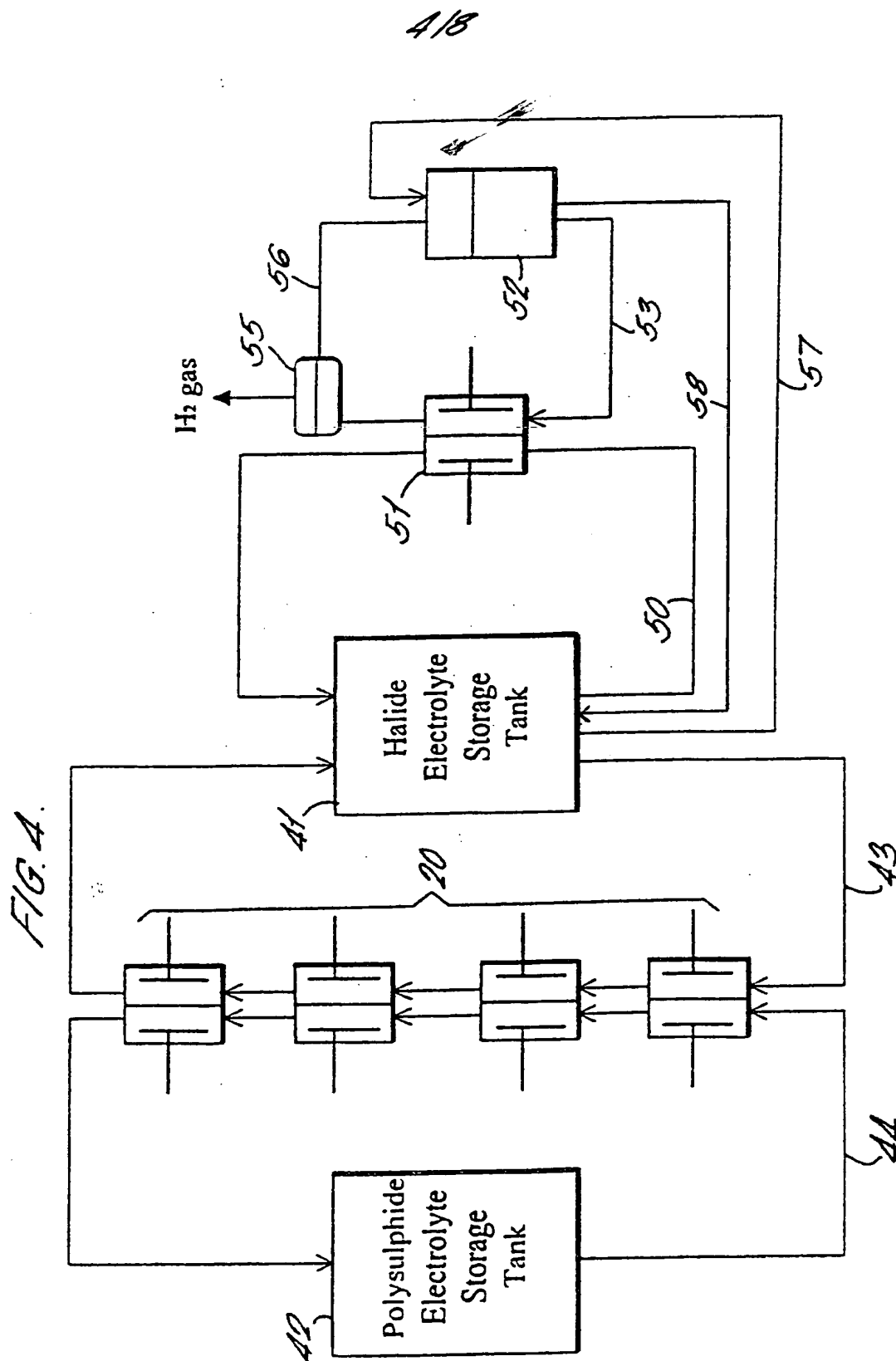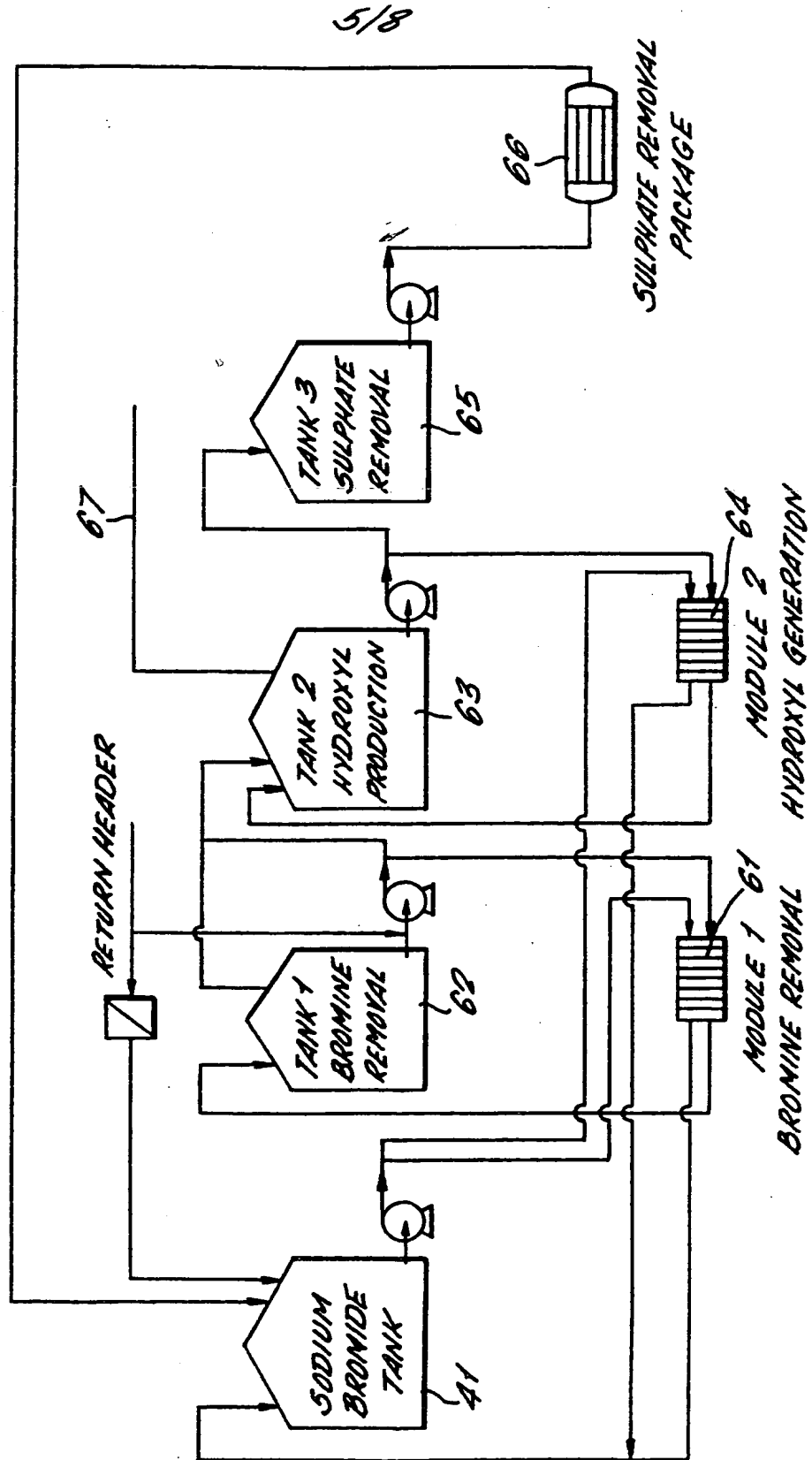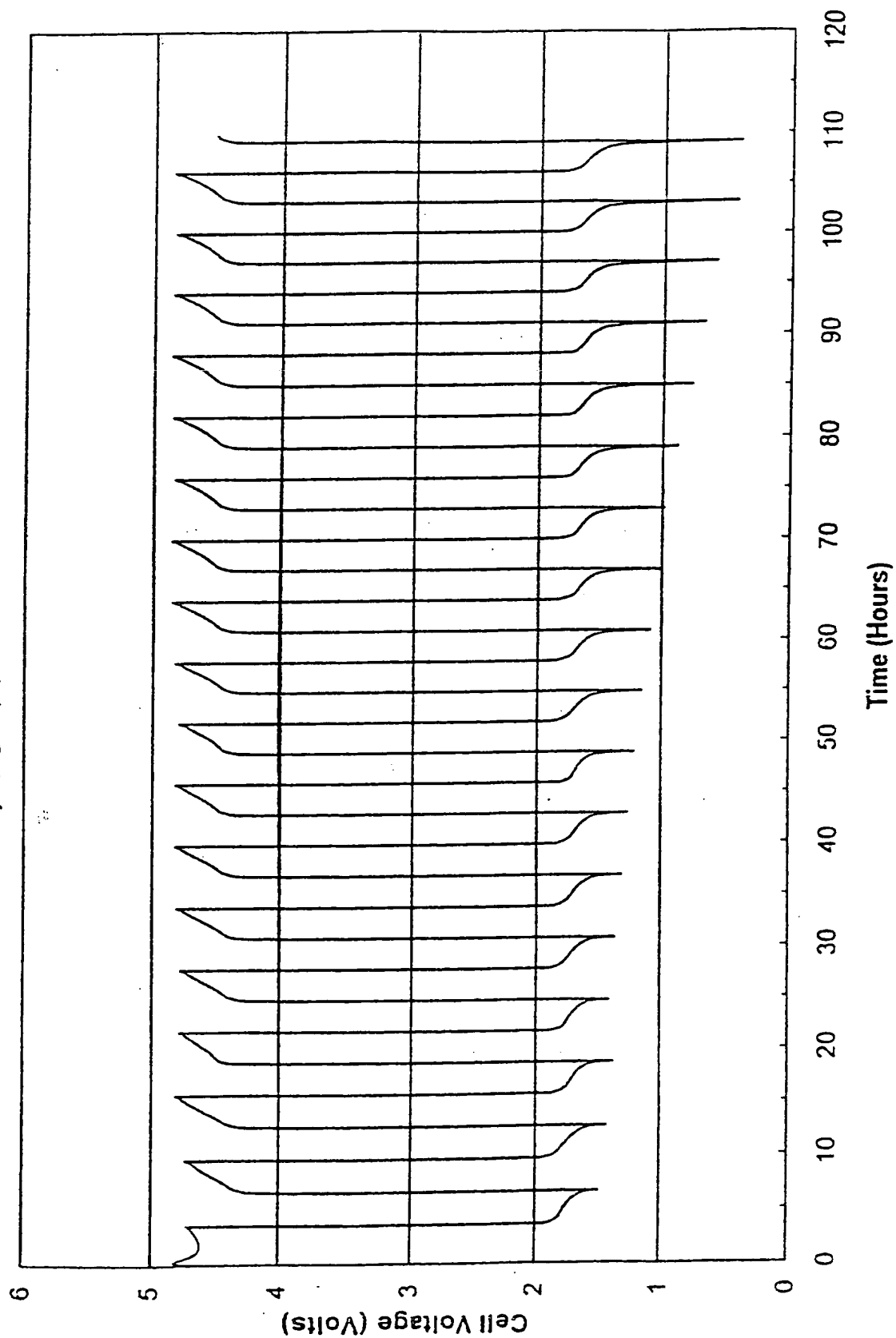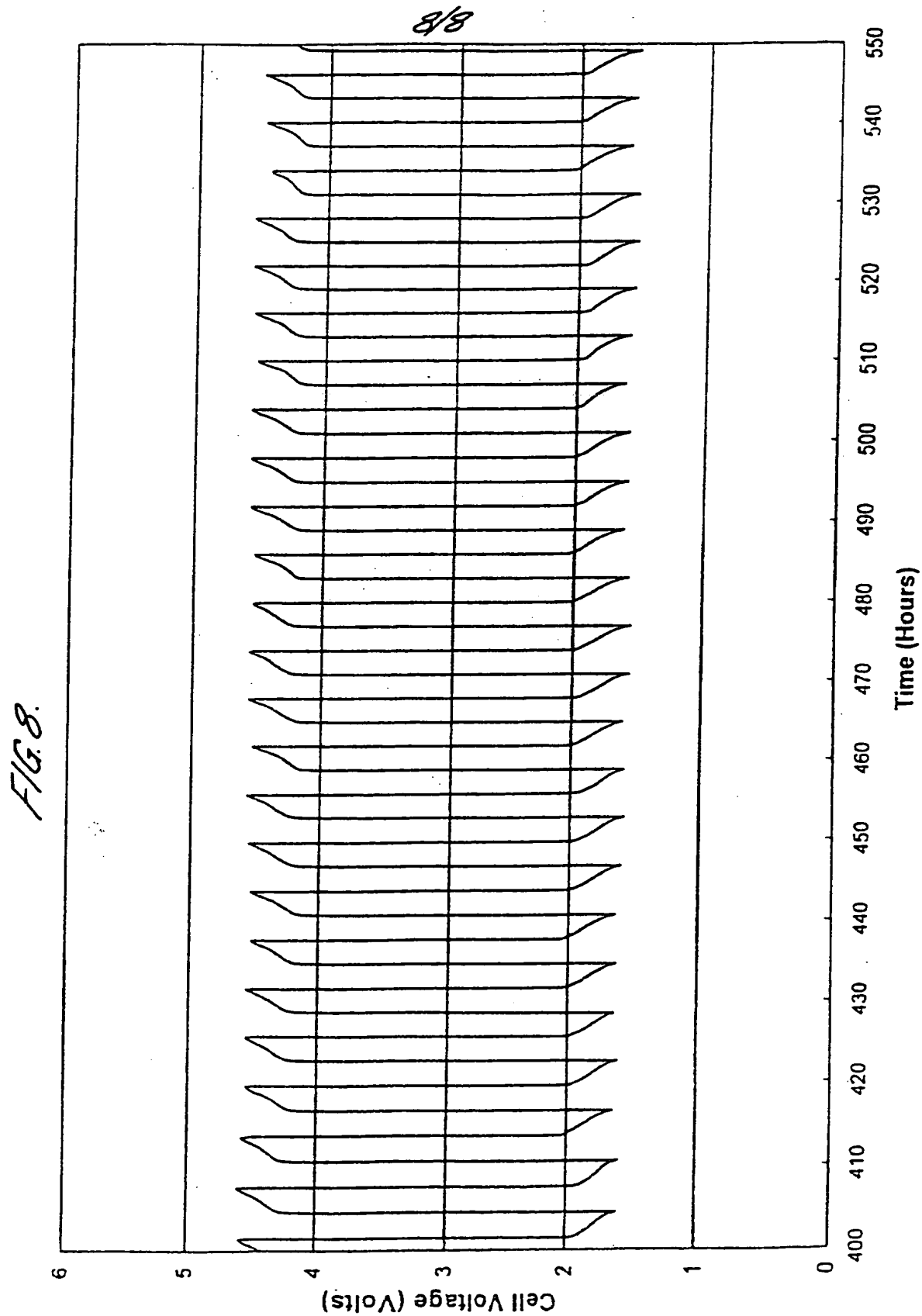
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FIG. 1A.

FIG. 1B.

FIG. 2.

FIG.3

FIG.4

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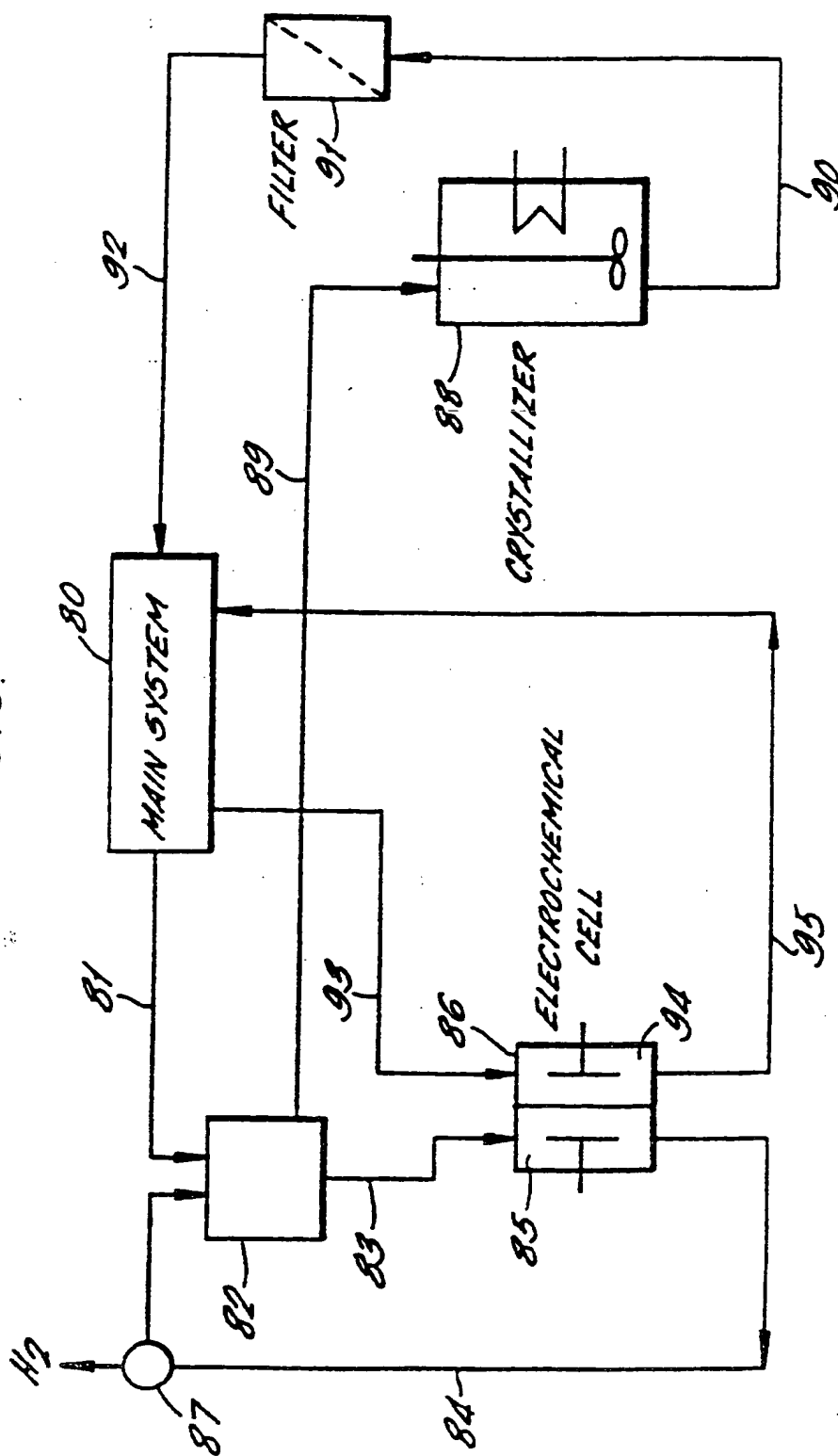FIG.5.

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FIG. 6.

FILTER 91

92

90

CRYSTALLIZER 88

89

MAIN SYSTEM 80

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95

82

83

ELECTROCHEMICAL CELL

86

94

85

95

84

87

H₂

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FIG. 7.

Time (Hours)

Cell Voltage (Volts)

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FIG.8.

Cell Voltage (Volts)

Time (Hours)

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   H01M8/04   H01M8/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, CHEM ABS Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 October 2000	24/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Battistig, M

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